Faculty of Resource Science and Technology

PREPARATION OF CHEMICALLY MODIFIED SAGO BARK FOR OIL SORPTION

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Declaration

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning. I hereby declare that this project is the work of my own excluded for the references document and summaries that have been acknowledge.

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(RANTHI RASTHULINI BINTI AHMAD)

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LIST OF ABBREVIATIONS

EFB	Empty Fruit Bunch
MEFB	Modified Empty Fruit Bunch
SB	Sago Bark
ESB	Esterified Sago Bark
NaOH	Sodium Hydroxide
SAH	Succinic Anhydride
CaO	Calcium Oxide
DMAP	4-(dimethylaiono)pyridine
UEO	Used Engine Oil
SEM	Scanning Electron Micrograph
FTIR	Fourier Transform Infrared
ml	Milimeter
g	Gram
SA	Stearic acid

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Preparation of Chemically Modified Sago Bark for Oil Sorption

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ABSTRACT

Natural fibers have proved to be an excellent to clean up oil spill. The main disadvantage of the natural fibers to be used as clean up oil spill is their hydrophilic nature. Empty fruit bunch (EFB) and sago bark (SB) have been used as a raw material of this study because of its abundance, accessibility and suitability. EFB and SB were modified with esterification by steric acid in the presence of catalyst. Esterifications of fibers were done to reduce the hydrophilicity and thereby increasing the sorption characteristics. The SB and esterified sago bark (ESB) have been subjected to FTIR, SEM, density test, buoyancy test and hydrophobicity test to characterize the chemical and physical constituents. A detailed investigation on the oil sorption characteristics of SB and (ESB) has been carried out. Sorption test were conducted in dry system, wet static system and wet dynamic system. ESB has shown higher sorption capacity than SB. Hydrophilicity of the fibers decreased upon modification, which decrease water uptake and increase oil uptake.

Keyword: Oil Spill, Sago Bark, Esterification, Oil Sorption, Hydrophilicity, Hydrophobicity

ABSTRAK

Gentian asli telah terbukti sesuai untuk menyelesaikan masalah tumpahan minyak.Kelemahan utama gentian semula jadi dalah sifat hidrofilik.Tandan kosong(EFB) dan sagu kulit(SB) telah digunakan sebagai bahan mentah dalam kajian ini kerana kesesuaiannya selain mudah didapati dan banyak dihasilkan. EFB dan SB telah diubahsuai dengan pengesteran menggunakan asid sterik dengan kehadiran pemangkin. Pengesteran gentian telah dilakukan untuk mengurangkan hidrofilikdan dengan itu meningkatkan ciri-ciri penyerapan. SB dan esterified sagu kulit(ESB) telah dikaji melalui ujian FTIR, SEM, ujian ketumpatan dan ujian keapungan untuk manilai ciri kimia dan fizikal.Satu siasatan terperinci mengenai ciri-ciri penyerapan minyak untuk SB dan ESB telah dijalankan.Ujian penyerapan telah dijalankan dalam sistem kering, sistem statik basah dan sistem dinamik basah. ESB telah menunjukkan kapasiti penyerapan yang lebih tinggi daripada SB. Hidrofilik gentian menurun setelah pengubahsuaian,yang mengurangkan pengambilan air dan meningkatkan pengambilan minyak.

Kata kunci: Tumpahan minyak, Sagu kulit, Pengesteran, Penyerapan minyak, Hidrofilik, Hidrofobik

CHAPTER 1

Introduction

Oil spills over land, river or ocean has become a great and ever-increasing environmental problem (Wei *et al*., 2003). Oil spill occurs over the seas, water bodies and land surfaces due to tanker disasters, equipment breaking down, accidents and natural disasters during production, transportation, storage and use of oil (Praba Karan *et al.,* 2011).

Many methods have been used for recovering the oil spilled. *In situ* burning (Toyoda,2000), polymer material (Praba Karan *et al.*, 2011), oil-degrading bacteria, soap, and oil dispersion (Praba Karan *et al.*, 2011) are some of the common practice used to clean up the oil spill. However, these techniques have some limitations. *In situ* burning is ineffective because of the logistical difficulties of picking up oil from the sea surface and storing it prior to final disposal on land (Toyoda, 2000). Polymer material have high oil sorption capacity and low water uptake, and hence these sorbents are ideal materials for oil recovery from the water surface (Geralddeschamps and Marie., 2003). Despite the superior oil sorption properties their poor biodegradability makes them less attractive compared to some natural oil sorbents (Praba Karan *et al*., 2011).Oil dispersion may cause problems due to their toxicity effects of component release from the chemicals (Praba Karan *et al*., 2011).

Another potential oil removal technique is via adsorption process. Adsorption is recognized as an inexpensive, easy and effective technique when a good sorbent is used. Sorbents can be divided into three basic categories which are natural organic, natural inorganic, and synthetic. The examples of organic natural sorbent are peatmoss, straw, hay, sawdust, ground corncobs, feathers, and other carbon products (Aboul-Gheit *et al*., 2006). Natural inorganic sorbents include clay, perlite, vermi- culite, glass, wool, sand, and volcanic ash (Aboul-Gheit *et al*., 2006). Synthetic sorbents such as polypropylene and polyurethane are the most commonly used commercial sorbents in oil-spill cleanup, due to their oleophilic and hydrophobic characteristics (Sun *et al.*, 2003).

The application of natural sorbent materials is an attractive method for combating of oil spill pollution mainly due to their low costs (Saito *et al*., 2003) high effectiveness (Praba Karan *et al*., 2011) and biodegradability (Choi *et al*., 1993).Despite their advantages, many natural fibers suffer low hydrophobicity and buoyancy, and therefore only suitable for oil removal in the absence of water (Ali *et al*, 2012). In response, many studies have been conducted on methods to improve the oil removal efficiency of natural sorbent by mean of alkalization (Abdullah *et al.*, 2010), acetylation (Adebajo *et al.*, 2004) and esterification (Banerjee *et al.*, 2006).

Sarawak generated significant amount of agricultural waste from palm oil and sago processing industries. About 30,000 tonnes sago flour and their residue generated by sago processing mills annually (Wahi *et al.,* 2010). Meanwhile, oil palm industries generates 12.4 million tones of empty fruit bunches (EFB) annually. The agricultural waste residues substantially composed of lignin and cellulose (Quek *et. al.*, 1998) and currently are underutilized. Sago bark, for instance, tends to be discharged into rivers and cause environmental contamination.

In view of the need to find efficient, low cost oil sorbent from locally available resource, sago bark and empty fruit bunch was chosen as the raw material in this study. Chemical modification via esterification was conducted on SB and EFB to further enhance the oil removal capacity. A systematic study was carried out to understand the behavior of sago bark (SB) and empty fruit bunch (EFB) before and after the chemical modification. Sorption was carried out using used engine oil.

1.1 Problem Statement

Oil spills are a global concern due to their environmental and economical impact. The oil waste is usually discharged into the river, lake and marine environment which caused much pollution to our environment. Therefore, it is important to find alternative way to reduce this problem. In Malaysia, oil palm and sago is one of the most important commercial crops. However, they produce a large amount of waste that can gives impact on our environment which would eventually affect human health and welfare.

The use of waste such waste and low cost cellulosic biomass such as oil palm empty fruit bunch and sago waste would significantly reduce the cost of oil spill cleanup. The used of chemically modified EFB and SB for oil absorption is one of the ways to reduce the oil spill in the environment. The performance of the chemically modified EFB and SB as an oil absorption in the treatment of oil spill is one way to reduce their impact due to high production.

1.2 Objectives

1. To prepare chemically modified EFB and SB as an oil absorbent through esterification.
2. To study the characteristics of raw and modified EFB and SB as oil sorbent.
3. To determine the optimum SB esterification condition.
4. To conduct oil absorption study using raw and modified SB.

CHAPTER 2

Literature Review

2.1 Oil Spill and their consequences

Oil spill imposes a major problem for the environment especially to the river and ocean. Oil spill occurs due to human activities that gives effect to different ecosystem. Oil is a very complex mixture containing various chemical with different properties. The spilled oil has higher potential to cause ecological effects. The physical effects of the spilled oil, plus the less visible effects caused high concentrations of toxic components released from the oil that will affect the some marine resources in localized area (Lewis, 2001).

According to Praba Karan *et al.* (2011), when oil comes in contact with water, it forms oil-in-water emulsion or floating film that needs to be removed before it is discharged into the environment. A very low concentration of oil could cause toxic to the microorganism that is responsible to undergo biodegradation of sewage process.

Cleaning up oil spill is difficult and caused economical problem. It is uneconomical to store large quantities of sorbent materials that are used to clean up the oil spill and their disposal (Praba Karan *et al.*, 2011). Therefore, there is a need to look into alternatives and investigate a low-cost method which is effective, economics, and applicable to industries (Quek *et al.*, 1998).

2.2 Type of Sorbents for Oil Removal

Different materials have been used for oil spill cleanups. Sorbents particularly caught the attention due to the possibility of collecting and completely removing the oil spill (Radetic *et al*., 2008). Sorbents are required to show high sorption capacity, high hydrophobicity and oleophilicity, high uptake capacity, good buoyancy, adequate oil retention, biodegradability and preferably be reusable (Praba Karan *et al*., 2011).

Sorbents can be divided into three basic categories which are natural organic, natural inorganic, and synthetic (Aboul-Gheit *et al*., 2006). Polypropylene and polyurethane foam are the synthetic sorbent that most widely used sorbents for oil spill cleanup because of their highly oleophilic and hydrophobic properties (Praba Karan *et al*., 2011). Despite the superior oil sorption properties their poor degradability makes them less attractive compared to natural sorbents (Choi and Moreau., 1993).

Natural sorbents are derived either from plant and animal residues (organic sorbent) or minerals (inorganic sorbent). The organic sorbent includes peatmoss, straw, hay, sawdust, ground corncobs, feathers, and other carbon products (Aboul-Gheit *et al*., 2006). Natural sorbents has relatively high sorption capacity and comparable if not lower densities, environmental friendly and cost effective (Adebajo and Frost, 2004). Other advantages of natural oil sorbent are possibility of sorbent collection, higher oil recovery and relatively easy disposal (Abdullah *et al*., 2010).

A number of natural sorbents have been studied for use in oil-spill cleanup, e.g. cotton (Choi and Kwon 1993; Choi, 1996; Johnson *et al*., 1973), wool (Radetic *et al*., 2003), bark (Haussard *et al*., 2003), kapok (Hori *et al.,* 2000, Ghalambor 1995; Rowell, 1998) and rice straw (Sun *et al*., 2002). Natural sorbents such as milkweed and cotton have greater potential for oil spilled cleanup as they are able to absorb significantly more oil compared to the commercial synthetic sorbent material (Praba Karan *et al*., 2011).

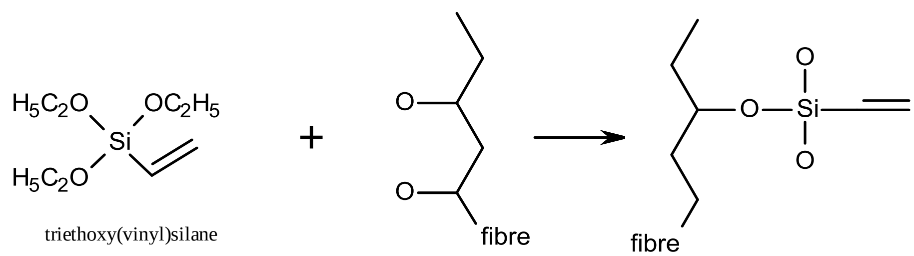
Natural sorbents, if used effectively, can be more efficient than synthetic products. Despite of their advantages, many natural sorbents suffer drawbacks in terms of high water uptake (Ali *et al*., 2012). High water uptake is associated with the low hydrophobicity or water repelling ability of the sorbents that will reduce the effectiveness of sorbent microporous structure to absorb oil due to high water uptake (Likon *et al*., 2013). Previous study also shows that low hydrophibicity also associated with low buoyancy.

2.2.1 Chemically modified natural sorbents

The main disadvantages concerning natural fibers are their susceptibility to moisture uptake, low hydrophobicity and low buoyancy (Sreekala and Thomas, 2003). The hydrophilic properties of the natural fiber must be modified before being utilized for oil removal. Mercerization, introduction of coupling agent, acetylation, latex coating, silylation and end peroxide treatment on fiber were done to enhance the hydrophobicity (Sreekala and Thomas, 2003).

With NaOH treatment, the hydrogen bonding inside kapok fiber is reduced via the hydroxyl group reduction through mercerization. The hydroxyl groups facilitate the hydrogen bonding with the carboxyl groups, such as fatty acids on the surface of the natural fiber (Abdullah *et al*., 2010).

The fiber surface modifications in chemical ways remove natural and artificial impurities that improve fiber-matrix adhesion. Previous study found that modification with silylation (Scheme 1) would strengthen material by less water adsorption (Sreekala and Thomas, 2003).



Scheme 1: Modification using tri-ethoxy vinyl silane coupling agent (Sreekala and Thomas, 2003)

2.3 *Metroxylon* Sagu

Metroxylon sagu which commonly known as sago belongs to Palmae family (Singhal *et al*., 2008). Sago grows widely on Sarawak's peat soil and identified as a great potential for commercial plantation and value added processing.

The importance of starch production by sago palm is mainly focused in the Asia-Pacific region and South East Asia (Wang *et al*., 1996). Sago starch is a valuable source of carbohydrate and it is widely used in food industries. It is a species from which useful quantities of starch-rich flour can be extracted from stem tissue by shredding and sedimentation in water (Wina *et al*., 1986).

Sago is an extremely hardy plant, thriving in swampy, acidic peat soils, submerged and saline soils where few other crops survive, growing more slowly in peat soil than in mineral soil (Awg Adeni *et al.,* 2010). Research on sago should be explored as crop has several advantages such as economically acceptable, relatively sustainable, environmentally friendly, uniquely versatile, vigorous, and promoted socially stable agro forestry systems (Stanton,1993).

2.3.1 Sago Waste

Sago waste is an inexpensive, copious fibrous residue left behind after most of the starch has been washed out of the rasped pith of the sago palm (Singhal *et al*., 2008). It is a starchy lignocellulosic by-product generated from pith of sago after starch extraction (Awg Adeni *et al*., 2009). Microscopic examination revealed a large number of starch granules to be trapped within the lignocellulosic matrix (Chew and Shim, 1993).The waste contain approximately 66% starch and 14% fibre on a dry weight basis of which about 25% is made up of lignin (Chew and Shim, 1993).

Sago waste which largely composed of cellulose and lignin (Vickineswary *et al*., 1994) is both a waste and a pollutant has some potential as a biosorbent. Moreover, sago wastes are difficult to handle due to high humidity and starch content (Awg Adeni *et al*., 2010).

Two types of solid sago waste are SB and sago hampas. SB is produced during the extraction of sago powder and is generated from debarking process. A lot of sago bark left behind at the powder extraction plant and commonly destroyed through open burning. Sago hampas is the starchy, fibrous portion of sago pith and generated during sieving and purification sago starch. For every tonnes of dry sago flour produced, 0.5 tonnes of sago bark and 3 tonnes of hampas are generated (Abd Rahman, 2005). At present, SB has been disregarded. They are not fully utilizes into a valuable products.

2.4 Empty Fruit Bunches

Another type of agricultural waste is empty fruit bunch (EFB). EFB produce from palm oil. Palm oil (*Elaeis guaineensis*) has become the most important economic plantation crop in Malaysia. Palm oil mills produce a large amount of solid wastes during production. The remainder of the oil palm consists of huge amount of lignocellulosic materials such as oil palm fronds, trunks and EFB **(Figure 1)** (Norhayati, 2006). EFB is a remaining material of the fruit bunches after the fruits have been stripped into the following steaming process at the oil palm mill. EFB is the suitable raw material for recycling because it produced in large amount of quantities in localized area.

Figure 1: Empty Fruit Bunches

Malaysia is the largest oil palm producer in the world and generates one of the most abundant residues namely EFB, amounting to 12.4 million tonnes annually (Tanaka *et al.,* 2004). In Malaysia, oil palm is one of the most important commercial crops. In 2006, Malaysia produced about 70 million tons of oil palm biomass, including trunks, fronds and empty EFB (Yacob,